

# Neutral Dissociation of Hydrogen Following Photoexcitation of HCl at the Chlorine *K*-Edge

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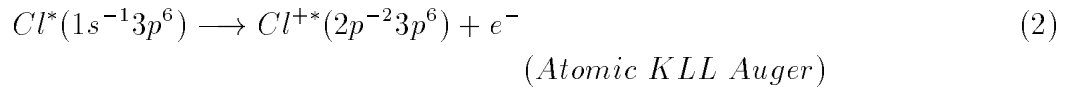
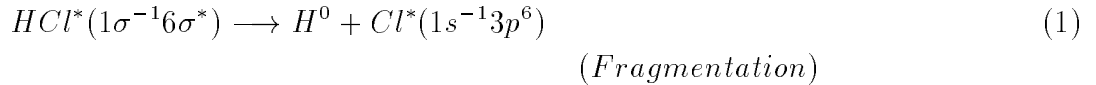
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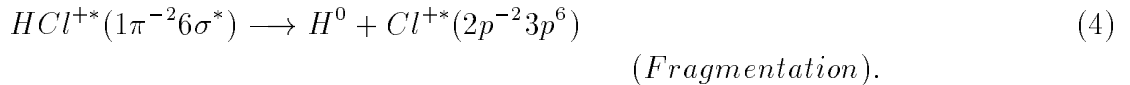
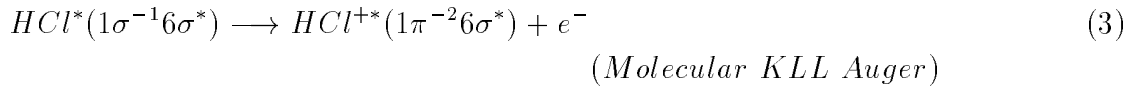
Time-of-flight mass spectroscopy was used to study the relaxation dynamics of HCl following photoexcitation in the vicinity of the Cl K-edge ( $\sim 2.8$  keV) using monochromatic synchrotron radiation from B.L. 9.3.1. At the lowest resonant excitation to the  $6\sigma^*$  antibonding orbital, almost half of the excited molecules decay by emission of a neutral H atom, mostly in coincidence with a highly charged  $\text{Cl}^{n+}$  ion. The present work demonstrates that neutral-atom emission can be a significant decay channel for excited states with very-short lifetimes (1 fs).

As a simple diatomic with deep-core electrons, HCl was chosen for the present experiment because the core-level spectroscopy is well understood and because of the relatively few ion fragments possible, facilitating interpretation of the subsequent mass spectra. Also, electron-spectroscopy measurements for the shallow-core Cl 2p level of HCl as well as ion-spectroscopy measurements of the K-shell of Ar, which is iso-electronic with HCl, are available for comparison. Fig. 1 shows the ratio of the yield of  $\text{H}^+$  to the sum of the yields for all Cl charge states. On the  $6\sigma^*$  resonance Fig. 1 shows a drop in the  $\text{H}^+/\text{Cl}^{n+}$  ratio of about 40%. The magnitude of this effect is particularly surprising considering the short lifetime of a Cl K-shell hole (1.1 fs), and that there is enough energy in the system to form highly charged chlorine ions (up to  $\text{Cl}^{6+}$ ).

Corresponding to the decrease in the  $\text{H}^+$  yield is an increase in the relative yields of  $\text{Cl}^{3+}$  and  $\text{Cl}^{4+}$ , suggesting an association with formation of neutral hydrogen on resonance. These results suggest one or some combination of the following types of decay paths following resonant excitation of HCl:



or



Auger decay of the two L-shell holes leads to the formation of a  $\text{Cl}^{3+}$  ion. Dissociation prior to or after the relaxation of the K-shell hole is the key point of comparison in these mechanisms.

From the present experiments, it is impossible to determine which of these paths is more probable. The higher electron density around the H atom in the excited  $\sigma^*$  orbital, coupled with the fact that the H atom has very little time to move during the lifetime of the core hole, opens up the possibility that the excited electron in the  $\sigma^*$  orbital remains as a spectator electron, localized around the H atom. The spectator electron which is not ejected in the subsequent Auger decay, thus allows the H atom to fragment as a neutral. Electron spectroscopy of the KLL-Auger electrons would reveal if the Auger decay takes place from an atomic or molecular species, and in the case of molecular decay, if the electron in the  $\sigma^*$  orbital is a spectator or participator in the Auger decay, thus determining if the dissociation of the molecule occurs on the same time scale as the Auger decay. Studies done at the Cl L-edge of HCl indicate that at the  $\text{Cl } 2p \rightarrow 6\sigma^*$  resonance, dissociation followed by Auger decay of the atomic Cl fragment is the dominant decay path. However, the fact that a Cl K-shell hole has a shorter lifetime than an L-shell hole by a factor of about 6 [a K-shell hole has a lifetime = 1.1fs (0.6 eV); for an L-shell hole the lifetime is 6.6 fs (0.1 eV)] may allow Auger decay to compete more favorably as the first step in the decay process.

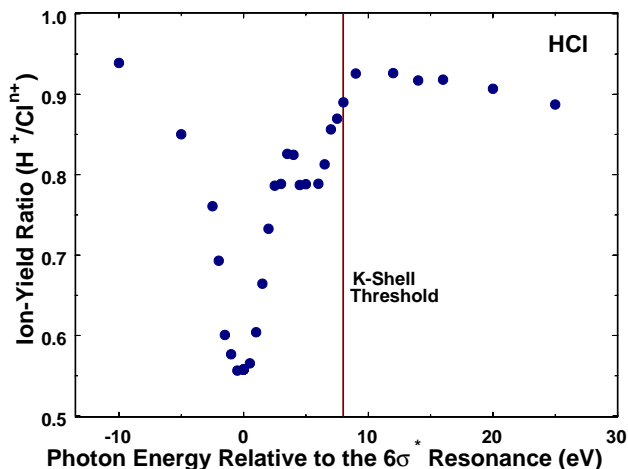


FIG. 1. Ratio of hydrogen ions detected to the sum of all chlorine ions detected in singles mode.

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